

PLASMATRON NATURAL GAS REFORMING

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Introduction

Low-current plasma discharges have been tested for reformation of natural gas. Experiments were carried out using both homogeneous (non-catalytic) and heterogeneous (catalytic) conditions at power levels of 200 and 700 W. Byproducts of the reforming process were hydrogen, CO, and light hydrocarbons. Hydrogen yields were around 40% for homogeneous conditions with 40% energy efficiency whereas for catalytic reforming it was 70% with an energy efficiency of 90%. In addition, the effect of stratification (inhomogeneous air/fuel mixtures) were investigated. This paper presents comparison between models and experiments carried out with air. Future papers will present results using oxygen-enriched air, and CO₂ enriched-air. Results of modeling that involves simple CFD simulations without combustion have been used to calculate the mixing time. The chemistry is modeled using the Partially Stirred Reactor and Perfectly Stirred Reactor options of Chemkin.

Plasma Reforming. Experimental results of plasma reformation and the reformation setup have been described before^{1,2}. The experiments that were modeled were carried with commercial grade natural gas with a power of 250 W, and a flow rate of 0.3 g/s, with O/C ratio ~ 1.1. Although some of the experiments were carried out with a catalyst downstream from the plasma, the results commented in this paper were for homogeneous reforming.

Experimentally it was determined that strong stratification of the air fuel mixture in the plasma zone was required for reaction initiation. Premixed air/methane mixtures could not be started under the conditions tested.

Models for plasmatron methane reforming. To understand the plasmatron reformer several models were developed. They included PFR as well as Partially Stirred Reactor (PaSR).

Ignition delay in the presence of radicals

In order to determine the effect of radicals that are produced by the nonthermal plasma, calculations were performed using CHEMKIN 3.7 Plug Flow Reactor. Multiple radical concentrations were used, with the rest of the well-mixed air/methane mixture. Multiple temperatures were considered. The results from the calculations are shown in Table 1.

Three radical types were used: atomic oxygen (O), hydroxyl (OH) radical, and atomic hydrogen (H) radicals, for initial temperatures from 600 to 1000 K. Shown in table 1 is the ignition delay, defined as the time for consumption of 10% of the fuel. However, the reaction, once it starts, is so fast (stiff chemistry) that the 10% assumption is not important.

The results in Table 1 indicate that even very large concentrations of radicals at low temperature do not substantially change the ignition delay. The radical concentration assumed in table 1 is very large, much larger than what could be expected for the conditions of the experiment. From the simulations it is clear the radicals recombine, raising slightly the air/methane temperature. This increase in temperature occurs very quickly (on the order of 10's of microseconds). The slightly increase in temperature is responsible for the relatively small effect in the ignition delay.

Table 1. Ignition Delay Time (In Seconds) For Various Radicals For Multiple Air/Methane Temperatures.

Methane homogeneous ignition delay time (s)

Initial Temperature	600 K	700 K	800 K	1000 K
No radicals	>1000	920	12.5	0.31
[O]=3e-4	>1000	195	4.3	0.23
[O]=3e-5	>1000	515	8.1	0.30
[OH]=3e-4	>1000	290	5.7	0.29
[H]=3e-4	>1000	240	4.9	0.25
[O]=[H]=3e-4	>1000	140	3.5	0.23

Model Using Partial Stirred Reactor

The plasma was modeled by using a high temperature zone that started local reaction and then through mixing carried the reactions to the rest of the air/fuel mixture.

To simulate the inhomogeneities, the PASR model³ was used. The model allows for control of the mixing time. However, the code has limitation with respect to the number of input streams (two). This places a severe constrain in the capabilities of the model.

It is thought that the effect of the plasma is to raise the local temperature of the air/methane mixture in order to locally ignite the air/fuel mixture. The actual temperature of the local regions is not known. Possible energy distribution are shown in Figure 1. The plasma power requirement is shown in this Figure as a function of the temperature of the hot zone, with the fraction of the hot zone as a parameter. Different fractions of hot-zones (with respect to the total gas flow) are assumed: 1%, 5%, and 10%. As the temperature of the hot zone increases for a given hot-zone fraction, the power required increases. Because of changes of the heat capacity as a function of temperature, the lines are not quite linear (although approximately linear). When the fraction of hot particles increases, the power increases. Figure 1 was calculated for flow rates typical of the plasmatron operation, about 0.4 g/s methane and O/C = 1.

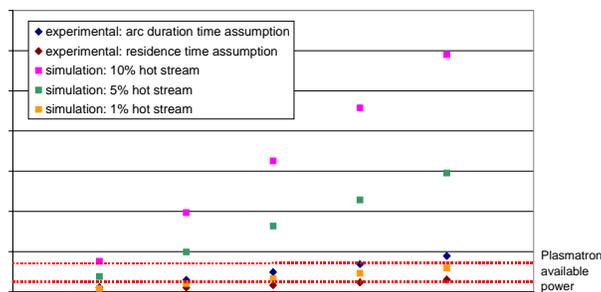


Figure 1. Power requirement as a function of the temperature of the hot zone, for several hot zone fractions.

Calculation of the PASR for the type of hot zone fraction and hot zone temperature shown in Figure 1 are given in Figure 2. These are the results of homogeneous mixture of methane and air, with a fraction of the zones at high temperature, for different ratios of mixing time to residence time, for different values of the hot zone temperature. It is assumed that 10% of the air/methane mixture is in the hot zone.

There is a maximum of the hydrogen production as a function of the ratio between the mixing time and the residence time. This can be understood by realizing that if the mixing is too fast, the hot zone enthalpy is divided with the rest of air/methane, with an increase in temperature but with little reaction. On the other hand, if the mixing time is too long, too many cold zones never get the energy required for reaction initiation, and conversion is poor.

The residence time in the plasmatron region is on the order of 1 ms. Calculations of the mixing time, by both back-of-the-envelope and CFD calculations (in the absence of chemistry), indicate that the mixing time in the plasmatron is on the order of 100 microseconds.

The results are in relatively good agreement with the experiments. However, the power required by the calculations is substantially larger than the one that is determined experimentally. While the calculations assumed about 2.5 kW power (10% as hot zone fraction with a temperature of about 5000 K), the experimental results are obtained at about one order of magnitude smaller powers.

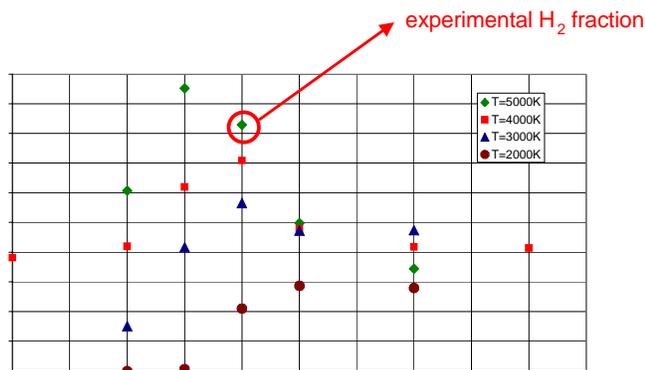


Figure 2. Hydrogen concentration (by mass) as a function of the ratio between the mixing time and the residence time, for residence time of 1 ms. Results are plotted for different temperatures of the hot zone.

Table 2 shows the results from the experiments as well as from the calculations. Because the PaSR model in Chemkin does not calculate volume fractions, Table 2 shows mass concentrations. The first row shows the experimentally determined H₂, CO, H₂O and CO₂ mass fractions. The last three rows show the results for the PaSR model assuming that a fraction of the particles in the PaSR model are at 5000K. The fraction of particles at this temperature is varied from 1% to 10%.

The hydrogen mass concentration is comparable to those in the experiment. However, the measured concentrations of water (experimentally derived from mass balance) CO₂ are substantially higher than in the model.

In addition, the power required for good comparison in the experimentally and calculated values of the hydrogen mass balance (about 5% particles at 5000K) is substantially higher (~1500 W from Figure 1) than the power in the experiment.

We assume that the reason for the difference in the results is due to the limited capabilities of the PaSR model to handle non-uniform air/fuel mixtures,

A recently released version of CHEMKIN 4.0 has substantially enhanced PaSR modeling capabilities. Calculations will be carried out to determine whether better agreement between experiment and the model can be obtained. The greater flexibility in establishing particle distribution functions (PDF's) at user-defined temperatures allows the model to represent closer the experiment. Presently, our understanding of the process is that in a non-uniform air/natural gas

mixture the plasma starts the reaction in zones that have O/C ratios that are favorable for reaction (i.e., near stoichiometric combustion). The heat generated in these zones increase the temperature, through mixing, of the other zones. Once hot, reaction in these zones can take place.

Summary

In order to understand the natural gas plasma reformation process, modeling has been undertaken. At the present time we believe that processing requires air/fuel stratification, combustion of a fraction of the fuel in regions of appropriated O/C ratios, mixing with the unreacted mixture. This process generates combustion products with energy and fuel loss that may not be recoverable.

The nonthermal plasma processing is good, however, for initial processing of hydrocarbons fuels. Controlled preprocessing with the use of nonthermal plasmas could lead to a decrease in the amount of catalyst required for initial gas preheating, decreasing the problems with hot-spots in the catalyst bed (having the hot spot in the homogeneous zone), and decreasing the amount of carbon formation and decreased methane concentration and free oxygen in the reagents at the location of the catalyst.

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References

- (1) *Plasma Catalytic Reforming of Methane*, L. Bromberg, D.R. Cohn, A. Rabinovich and N. Alexeev, *Int. J. Hydrogen Energy* **1999** 24, 1131
- (2) *Plasma Reforming of Natural Gas*, L. Bromberg et al., submitted for publication, *Int Journal Hydrogen Energy*.
- (3) Reaction Design, PaSR Application User Manual, CHEMKIN Collection 3.7.1, 2003.

Table 2. Comparison of Mass Concentratatino of H₂, CO, H₂O and CO₂ Between Experiment and Calculations, For 250 W Plasma Power and O/C ~ 1, with Natural Gas.

O/C=1 t _{res} =1ms t _{mix} =0.1ms	Power input [kW]	H ₂	CO	H ₂ O	CO ₂
Exper. results	0.6	.60%	5.0%	7.0%	4.0%
10% particles @ 5000K	3	.80%	5.7%	1.8%	0.3%
5% particles @ 5000K	1.5	.45%	3.0%	1.0%	0.2%
1% particles @ 5000K	0.3	.03%	0.3%	0.1%	.05%